

## **SUMMARY: ACCELERATE SALT RETRIEVAL, PROCESSING, AND DISPOSITION AT SAVANNAH RIVER SITE**

### **Introduction**

The Department of Energy (DOE) technology selection for Savannah River Site (SRS) High-Level Waste (HLW) salt solution processing was completed and the Salt Processing Environmental Impact Statement Record of Decision was issued in October 2001. The Record of Decision designated Caustic Side Solvent Extraction (CSSX) as the preferred alternative to be used to separate cesium (Cs) from HLW salt. In parallel, DOE is evaluating the implementation of other salt processing alternatives for specific waste portions that would not need to be processed in the CSSX facility. The evaluation of alternatives and potential operations will be undertaken to maintain operational capacity and flexibility in the HLW System and meet commitments for closure of HLW tanks.

The Savannah River Operations Office strategy relies on a graded approach to salt processing. The new integrated Salt Disposition Strategy is to:

- Treat low-curie salt waste and dispose at Saltstone,
- Create an Actinide Removal Process to enable disposal of additional low curie/high actinide salt waste and potentially provide actinide removal for the high curie demonstration CSSX facility,
- Dispose of high-curie salt waste by removing Cs in a small scale demonstration CSSX processing facility, and
- Tailor follow-on high-curie salt waste processing capability depending on the success of early low-curie salt disposal.

To accelerate completion of the SRS HLW mission, Office of Science and Technology (EM-50) in partnership with SRS, has initiated a project entitled "Accelerate Salt Retrieval, Processing, and Disposition at Savannah River Site." The primary objective of this alternative project is to accelerate salt processing by demonstrating alternative technical approaches that can be deployed near-term, using existing facilities whenever possible, and reduce the cost and time required to complete the SRS HLW mission. Success in this alternative project will significantly reduce, or may eliminate entirely, the need to expand capacity of the initial Salt Waste Processing Facility (SWPF) and will serve to reduce technical and programmatic risk in the SRS salt processing program.

Definition of technical initiatives is ongoing with EM-50 and SRS HLW personnel. Proposed activities under this project are divided into four major areas. They are: 1) Improved Salt Cake Dissolution and Salt Chemistry, 2) Improved Strontium/Actinide Chemical Separation Processes, 3) Improved and Alternative Solid/Liquid Separation Methods, and 4) Alternative Cs Removal Processes. Since the focus of this summary report is on alternative processes for Cs removal, the other three activities will be discussed only briefly.

### **Improved Salt Cake Dissolution and Salt Chemistry**

Technology development needs for salt cake dissolution derive primarily from three fundamental requirements: salt cake dissolution must be conducted efficiently at lower cost (less equipment) than the current baseline, selective dissolution is required to separate high curie and low curie fractions, and the resulting dissolved salt solutions must be sufficiently stable to enable downstream processing without complications from solids formation. The preparation of low curie salt solutions is particularly critical for providing a near-term feed for Saltstone which will allow salt waste to be removed from the SRS waste tanks prior to startup of the SWPF.

### **Improved Strontium/Actinide Chemical Separation Processes**

During the past several years, the Salt Processing Project (SPP) examined the sorption of plutonium – and other radionuclides – by monosodium titanate under prototypical conditions for the process options. Preliminary estimates suggested that as much of 7 percent of the salt waste will require additional mitigation steps – e.g., dilution, extended processing tie, or addition of excessive sorbent – after treatment with the nominal amount of monosodium titanate.

Thus, alternative sorbents are being evaluated for improved actinide removal. The use of permanganate to selectively remove alpha emitters and strontium performed roughly equivalent to monosodium titanate. In the final quarter of fiscal year (FY) 2002, an overall assessment will be conducted of the viability of the permanganate technology for treatment of SRS waste and additional work will be conducted if required. Also, novel sorbents will be designed specifically to remove strontium and selected actinides. One set of studies in FY02 already generated a number of promising candidate materials based on strontium removal efficiency with actinide removal tests pending. This work includes the first-ever-reported synthesis of heteropolyniobates, a class of compounds predicted to offer superior actinide removal behavior based on structural considerations. Another study aims at developing the in situ formation of magnetite as a means of removing strontium and actinides.

In addition, deployment of this technology requires additional work to define the analytical instrumentation needed to verify process performance.

### **Improved and Alternative Solid/Liquid Separation Methods**

The research on the cross-flow filtration technology used as the baseline design includes both pilot-scale demonstration of the technology using simulated waste and successful experiments using actual HLW samples. The data suggest that the equipment will only marginally achieve the target performance and may well require frequent outages for cleaning. Thus, this technology may well force an extension of the operating lifetime for the facility and still represents a moderate technology risk.

To reduce the risk, the SPP continues to pursue alternate means of solid-liquid separation. The options under investigation include use of a high-shear, rotary cross-flow filter. Initial vendor

testing of the latter equipment using simulated waste shows significant promise of improved performance. Similarly, investigations continue on alternate process configurations that use chemical additives to achieve enhanced sedimentation in advance of the process facility. Such approaches may reduce the burden for the cross-flow filter, thereby substantially reducing the implementation risk. Finally, the decline in filter flux during cross-flow filtration may be overcome by using ultrasonically enhanced filtration.

### **Alternative Processes for Cs Removal**

A CSSX facility represents a significant capital cost and the opportunity for cost savings if the facility size can be reduced. Thus, efforts are underway to minimize the volume of salt solution needing Cs treatment by CSSX by identifying tanks containing Cs concentrations low enough that the solutions can be sent directly to Saltstone for disposal as low-level waste. Alternative, low-cost Cs-removal processes can potentially increase the volume of salt solution that could be sent to Saltstone by treating salt solutions that exceed the low curie limit (0.05 Curies/gallon). These processing approaches include in-tank batch treatments with inorganic sorbents and near- or in-tank sorbent columns. In addition, modifications to the CSSX baseline flowsheet (like higher salt feed concentration and reduced number of centrifugal contactor stages) will be evaluated and tested.

The following five specific tasks have been identified.

#### **I. Evaluate Alternatives to the CSSX Baseline**

The CSSX baseline process was designed to ensure a decontamination factor (DF) of 40,000 for Cs from salt solutions with 5.6 molar (M) sodium. Alternatives to the CSSX baseline are considered to improve capacity and to decrease cost of the facility. Some alternatives to the CSSX baseline include salt feeds up to 7.5 M sodium, reducing number of centrifugal contactor stages, and eliminating temperature controls. Increasing the sodium concentration of the salt feed would reduce the total volume of salt that must be processed, thus reducing the processing time or the facility size required. Reducing the number of centrifugal contactor stages and eliminating temperature controls reduce the footprint of the shielded facility resulting in lower cost, but do result in a lower Cs DF. In addition, some tanks may need low DFs such that batch extraction could be used for Cs removal. The alternatives will be evaluated with the goal of minimizing the overall cost of processing the salt waste and the most promising ones tested in the laboratory.

#### **II. Conduct Screening Tests and Actual Waste Demonstrations for Batch Cs Removal from Low Cs Simulants using Inorganic Sorbents/Precipitates**

Current plans at SRS propose discarding wastes containing radioactive cesium (Cs-137) concentrations less than 0.05 Curies/gallon either directly to the Saltstone Production Facility or processing to remove strontium and actinides in the Actinide Removal Process prior to processing at Saltstone. This option allows earlier removal and disposal of the waste,

reducing the risk and costs. Additional tanks contain wastes that only require modest Cs removal treatment efficiency to fall within the acceptable range for processing at Saltstone.

The first phase of testing will examine the sorbents in simulated waste solutions prototypical of the tanks amenable to this process option. A second phase of testing will examine the most promising materials using actual waste samples.

### III. Evaluate and Size Near and In-Tank Sorbent Column for Cs Removal from Low Curie Salt

An in-tank column uses the tank for shielding, minimizing the need for new facilities and, thus reducing the cost of processing waste. SRS has used sorbent columns suspended inside waste tanks in the past to remove low concentrations of Cs from supernatant solutions. The sorbent was a zeolite. Oak Ridge National Laboratories (ORNL) has demonstrated the use of near-tank columns of crystalline silicotitanate (CST) to remove Cs from a Melton Valley waste tank supernatant solution. The columns were small and shielded individually lowering the cost of the facility. Both methods showed sufficient decontamination to allow the treated solutions to be disposed as low-level waste. The sorbents can be released into a tank for mixing with sludge prior to vitrification or depending on the sorbent, converted directly to a waste form for disposal. The evaluation must consider past work, size of the column to allow heat removal from the loaded sorbent, size that could fit within the tank, handling and disposition of the loaded sorbent, and any other engineering aspects needed to decide between the two approaches. The work will involve modeling of columns using models developed for other programs.

### IV. Perform Non-radioactive Field Test of In-Tank or Out-of-Tank Cs Removal Column

Although in-tank and near-tank columns have been demonstrated in the past at SRS and ORNL, the columns and sorbent selected for this application will differ in size and operation. The columns identified in activity III above will require testing at full scale with non-radioactive simulants to confirm calculations and demonstrate loading and unloading sorbent. Further tests will be conducted using radioactive material to demonstrate Cs removal. The task will include installing the columns and tanks necessary for testing, preparing the simulant solutions required for the demonstration, and performing the column tests. The data from the tests will be analyzed and compared to model calculations to ensure proper operation conditions.

### V. Complete Demonstration of CST Up-flow Moving Bed Column

CST is a highly selective sorbent for Cs in waste solutions. CST is one of the primary backup technologies to CSSX solvent extraction. The pre-conceptual design basis fixed bed columns for CST Non-Elutable Ion Exchange were relatively large which raised a concern that a fully loaded column could contain approximately 5 million curies of Cs-137 and create an exceedingly intense radiation field with associated heat removal concerns if liquid flow

stops. In addition, incidents of column plugging and clumping of CST particles suggest that fixed bed columns may not be the most suitable for the salt processing program. Therefore, alternative column designs which address the above technical risks identified during the technology down-select process should be assessed.

The primary goal is to further test and evaluate conditions that avoid column plugging. This represents a viability issue since ion exchange resin loaded with Cs-137 provides a significant heat source within the column. The ability to move resin loaded with Cs-137 through the column after partial plugging has occurred would demonstrate that the system configuration is sufficient to either avoid the formation of clumps or to remove them after they have formed. Secondary goals include confirmation of mass transfer zone models, CST media attrition, and demonstration of system design and capabilities.

Completion of work activities III, IV, and V will address major vulnerabilities of the CST backup technology and move it closer to implementation should CSSX technology issues arise.